31

The Surface-force Theory of Rectification in Ionic Crystals

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1. *Unbalanced Electrostatic Force on the Surface of an Ionic Crystal.*

In ionic crystals, there is an array of net positive and negative charges which may be considered to be situated at the lattice points. If we take a crystal-plane where *similar* sets of ions are placed at regular intervals, it is evident, when we consider the surface layer and the next, that any ion on the surface layer will experience an unbalanced electrostatic force. If the first layer contains *all positive* ions, the next will have *all negative* ions. The unbalanced electrostatic force will then be directed towards the interior of the crystal. Alternatively, if the first layer contains *all negative* ions, the direction of the surface-force will be the other way. If again, a crystal-plane contains oppositely charged ions alternately, the electrostatic forces will act in opposite directions alternately. Applying the problem to the (100) face of a crystal of the NaCl type, Lennard-Jones, Taylor and Dent[1] have calculated the values of the electrostatic force for various points on the crystal surface.

[1] Lennard-Jones, Taylor and Dent., Trans. Faraday Soc., Vol. XXIV, 1928.

2. *The Cause of Rectification in Ionic Crystals.*

Of the two features of the current-voltage characteristic curves for rectifying crystals, namely, (1) asymmetry and (2) curvature, the first can be explained in the case of the ionic crystals in terms of the electrostatic surface-force. The surface-force retards electrons which flow in the same direction as and accelerates those flowing in a direction opposite to the electrostatic force. Thus when an alternating voltage is applied to the surface of such a crystal, the surface-force gives rise to a unidirectional current. The direction of the current depends on the direction of the electrostatic force on the crystal-surface. Considering the crystal-planes which contain *similar* sets of ions, if the first layer has all *positive* ions, the direction of the rectified current will be towards the interior of the crystal. If on the other hand, the first layer contains all *negative* ions, the rectified current will flow from the crystal to the "whisker" which is in contact with the surface of the crystal. If we call the rectified current positive, when it flows from the crystal to the "whisker," we would have negative rectification in the former case and positive rectification in the latter case. Both negative and positive rectification effects are therefore possible. In the planes which contain oppositely charged ions alternately, the "whisker" which is in contact with a large number of such ions, gives on an average, no rectification. In the case of a natural crystal, made up of many tiny crystals, the "whisker" may rest on any kind of planes exhibiting thereby positive, negative or no rectification. This is what has been actually observed, when several natural crystals of irregular form have been studied by the author in collaboration with Mr. A. K. Das Gupta. Only crystals of good crystalline form have shown rectification effects in the same direction.

To explain the curvature of the current-voltage characteristic curves, we should consider first the *local heating at the junction.*

As pointed out by Eccles,[2] the contact-resistance would gradually diminish with the increase of the voltage applied to the crystal due to the gradually increasing local heating at the junction. The increase of current due to this fall of contact-resistance can be more than proportionate with the increase of the applied voltage. The effect of this Joulean heating at the contact-point is the main cause of the curvature in the current-voltage characteristic curve.

The effect of strain on the crystal may also produce a slight curvature. The applied voltage causes a displacement of the ions from their positions of equilibrium. When the opposing elastic force is overcome by the applied field, the ions are set free. A part of the applied voltage is necessary to overcome the opposing elastic force and the rest is expended in driving the current through the crystal. All the ions are not however, set free at a definite voltage. There must always be a certain range of voltage within which all the different ions are liberated. This will evidently cause a bend in the current-voltage curve over this range of voltage. Dowsett[3] analysed the current-voltage characteristic curves for carborundum in a similar way.

Thus the electrostatic surface-force together with the heating effect at the contact-point and the effect of strain on the crystal can satisfactorily explain the two features in the phenomenon of rectification in the ionic crystals which do not show volume rectification.

3. *Different Degrees of Rectification on the same Surface.*

On a strictly plane surface of a good single crystal, the rectification effect must be more or less the same. The surface however is never plane. Invariably there are cracks and crevices

[2] Eccles, Proc. Phys. Soc. Vol. 22, 1914.

[3] Dowsett, Wireless Telephony and Broadcasting, Vol. II, Chap. II, p. 29.

and sometimes impurities, causing thereby varying degrees of asymmetry in the current-voltage characteristic curve. Again, the contact resistance may vary from point to point depending on the surface condition. These different values of the contact-resistance would result in different amounts of local heating. The curvature of the current-voltage curve is therefore expected to be different for different contact points ; for the curvature has been mainly attributed to the Joulean heating at the contact-point.

4. *Necessity of a small Contact Area for Rectification in the Ionic Crystals which do not show Volume Rectification.*

A small contact area for rectification is necessary in the case of the ionic crystals which do not show volume rectification. A large contact area means a large number of contact-points of varying degrees of rectification and the average gives a small effect. Besides, for some points, the contact resistance may be extremely small, causing more or less a short circuit. When the crystal is soldered on one side and a " whisker " is pressed at a point on the other side, we really observe the difference in the rectification effects for an extremely small and for a very large area of contact. The small area of the point contact controls the rectification.

5. *Variation of Resistance and Rectification Ratio with the Applied Voltage.*

How the resistance in either positive or negative direction changes with the increasing applied voltage depends on the shape of the current-voltage characteristic curve. In all our experiments, the resistance has been found to decrease with the increase in the applied voltage. This is explicable, for with the increase in the voltage, the Joulean heating at the junction is increased and the contact-resistance falls. Besides, the fall of

resistance may be expected, if the number of ions liberated increases[4] at a rate more than proportionate with the applied voltage. The rate of decrease of resistance is not the same for the two opposite directions. It is however, not possible to say definitely how the rectification ratio (the ratio of the difference in the rectified currents in the two opposite directions to the current in the low-resistance direction) should change with the increase of the applied voltage. In our experiments, the ratio has been found to increase in some cases and in some cases to decrease with the applied voltage. In some cases again, there has been an initial increase followed by a slight continuous decrease.

6. *Rectification observed with the Ionic Crystals (which do not show Volume Rectification) in contact with Pointed Crystals of the same Composition.*

The electrostatic surface-force is increased or decreased as the corresponding force at the pointed end is in the same as or opposite to that on the surface. Again a dipole induced in the pointed crystal reduces the electrostatic force on the surface of the crystal, thus decreasing the rectifying power. A small or sometimes a moderate value of rectification is thus expected. This is what has been found in our experiments. Eccles'[5] thermoelectric theory or Schottky's[6] electronic theory of rectification cannot explain the results of these experiments.

7. *Effect of Heating the Contact-point on the Rectifying Power.*

The interplanar distance in the upper layers of the crystal surface increases in the region of the contact, when the junction

[4] This is contrary to Joffe's idea. According to Joffe, Ohm's law holds in crystals. Hevesy, however, thinks that the degree of dissociation increases as the applied field is increased. *Vide* Joffe's Physics of Crystals, p. 94.

[5] Eccles, Proc. Phys. Soc., Vol. 25, 1915.

[6] Schottky, Zeit f. Physik., *14*, 1923.

is heated. The electrostatic surface-force is therefore slightly reduced in value. A slight diminution of the rectification effect in the ionic crystals (which do not show volume rectification) on heating the contact point is thus expected. The effect of the thermionic emission from the heating coil may have some effect, especially when the heating current is large. In the crystals, which show negative rectification, the first layer on the surface has been supposed, according to the surface-force theory, to contain only positive ions. The negative charges due to the thermions would cause a force in a direction opposite to that of the surface-force at the contact-point. This may reduce the rectification effect to a certain extent. When the heating current is large, it may sometimes be possible for the emitted thermions to cause a force larger than the surface-force, so that there may be a change in the direction of the rectified current on heating the contact point. In the case of the crystals which show positive rectification, the negative ions are on the first layer. The thermions get repelled and cannot produce any appreciable effect.

The experiments with Mr. Das Gupta have shown these features. Usually there is a decrease in the rectifying power when the contact-point is heated. With iron-pyrites (which shows negative rectification) in some experiments, a change in the sign of the rectified current on heating the contact-point has been observed, when the rectified current has been small.

8. *Effect of Heating the Crystal on Rectification.*

On heating a crystal there is an atmosphere of free ions in the crystal lattices. The photo-electrons which are normally embedded among the different lattices are set free, making the crystalline medium a better conductor. The electrostatic force on the surface layer of the crystal will thus be reduced. When the medium becomes sufficiently conducting, the surface-force may be extremely small. The rectifying power of some

crystals may thus be practically lost on sufficiently heating the crystals. Our experimental results and those of Flowers [7] showing complete or partial loss of the rectifying power of crystals on heating, can thus be explained. Frenkel-Jeffe's [8] theory can also explain the decrease in the rectifying property on heating.

9. *Effects of Ultra-violet Light and X-rays.*

Ultra-violet light produces electronic conductivity in dielectric crystals and liberates electrons inside the lattice. This internal photoelectric effect does not necessarily lead to an external effect. When the energy of the incident ultra-violet light is sufficient to produce the internal photoelectric effect, the surface electrostatic force will then be slightly reduced as the conductivity of the crystal is slightly increased owing to the electronic conductivity. When there is external photoelectric effect, the electrons emitted outside the surface tend to further reduce the surface electrostatic force in crystals which show negative rectification. With crystals which show positive rectification, the photoelectrons emitted outside are only repelled by the negative ions on the first layer and do not produce any effect. There will be a small decrease in rectification due to the internal photoelectric effect only which slightly increases the conductivity of the crystal.

The effect of X-rays will be similar and more pronounced. Inside and outside the crystal, the recoil electrons are produced by scattering. The conductivity of the crystal may thus be increased, reducing considerably the electrostatic force which determines the rectification effect.

The reduction in the rectifying property on exposure to ultra-violet light has been extremely slight in our experiments. There has been a very pronounced decrease in the rectification

[7] Flowers, Phys. Rev., 1909.
[8] Frenkel-Joffe, Phys. Rev., 39, 1932.

effect on exposure to X-rays. The results of Jackson's [9] experiments and our own experiments can therefore be explained.

10. *Rectification in Crystals having no Centres of Symmetry.*

The existence of volume rectification in carborumdum, zincite and silicon and the absence of it in the symmetrical crystals (*e.g.*, iron pyrites, galena, molybdenite, pyrolusite, bornite, etc.) which have been observed in the experiments with Mr. Dasgupta have suggested the classification of crystal-detectors into two groups : (1) ionic crystals having centres of symmetry, and (2) ionic or non-ionic crystals having no such symmetry. In the symmetrical ionic crystals, we observe the rectification due to the surface force and this is associated with point contacts. *The surface-force theory given in this paper refers to the symmetrical ionic crystals.* In the case of the ionic crystals having no centres of symmetry, we have to consider the volume rectification in addition to the rectification due to the surface force. The volume rectification can be tentatively attributed to the asymmetry in crystal structure as suggested by R. de L. Krönig [10] in his theory. According to Krönig, the crystal rectification is due to asymmetrical binding of the ions into positions of equilibrium by restoring forces not symmetrical for equal and opposite displacement. We can however explain the volume rectification in this way.

11. *Summary.*

A theory based on the existence of an unbalanced electrostatic force on the surface of an ionic crystal has been proposed in this paper to explain the phenomenon of contact-point rectification in symmetrical ionic crystals. It has been shown how this electrostatic force together with the heating effect at the contact point and the effect of strain on the crystal can satisfactorily

[9] Jackson, Phil. Mag., May, 1929.
[10] Krönig, Nature, March 2, Vol. 123, 1929.

explain the asymmetry and the curvature of the current-voltage characteristic curves for the symmetrical ionic crystals. The different degrees of rectification for the different point on the surface and the necessity of a point-contact have been explained. The following experimental results obtained with *symmetrical ionic crystals* are explicable according to the proposed surface-force theory.

(1) The positive, negative and no rectification effects observed in the natural poly-crystals.

(2) The fixed direction of the rectified current in crystals of good crystalline form.

(3) Rectification observed with crystals in contact with pointed crystals of the same composition.

(4) The effect of heating the contact-point on rectification.

(5) The effect of heat, ultra-violet light and X-rays on rectification.

In crystals having no centres of symmetry, the volume rectification has to be considered. There is evidence of very pronounced volume rectification in carborundum, zincite and silicon which can be explained according to Krönig as due to asymmetric binding of the ions, the restoring forces not being symmetrical for equal and opposite displacements.*

* An outline of the surface-force theory of rectification is recently published in *Nature*. Vol. 135, 1935, p. 148.

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